

THE ORIGIN, COMPOSITION AND HISTORY OF COMETARY ICES FROM SPECTROSCOPIC STUDIES; L. J. Allamandola, Space Science Division, NASA-Ames Research Center, Moffett Field, California 94035

The spectroscopic analysis of pristine cometary material provides a very important probe of the chemical identity of the material as well as of the physical and chemical conditions which prevailed during the comet's history. Concerning classical spectroscopy, the spectral regions which will most likely prove most useful are the infrared, the visible and ultraviolet. "Newer" spectroscopic techniques which have the potential to provide equally important information include nuclear magnetic resonance (NMR) and electron spin resonance (ESR).

This talk will summarize each "spectroscopy" with emphasis placed on the kind of information which can be obtained from each technique. The infrared should be the premier method of analysis as the mid-infrared absorption spectrum of a substance contains more global information about that substance's identity and structure than any other property. It was for this reason that the tabletop IR spectrometer quickly became the workhorse for industrial chemical analytical laboratories and has remained so for over forty years. The greatest strides in our understanding of the composition of interstellar ices, thought by many to be the primordial material from which comets have formed, have been taken during the past ten years or so, the period of time in which high quality infrared spectra of the interstellar medium have become available.

It must be kept in mind however that the interpretation of the infrared spectra of mixtures such as expected in comets is often (not always) ambiguous. Other non-destructive, complementary, spectroscopic measurements are required to characterize the material and probe for substances for which the infrared is not particularly well suited. While the mid- and far-IR span frequencies which correspond to skeletal vibrations in molecules and thus provide insight into the identity of chemical groups present, the ultraviolet, visible and near infrared span frequencies which correspond to electronic transitions and give insight into the molecular bonding structures present. In these regions absorption and emission studies are desirable. Absorption measurements have the potential to give an indication of the importance of conjugated bond systems, although sample porosity will almost certainly make the measurements difficult. More tractable will be luminescence studies. Measuring the luminescence excited by ultraviolet and visible photons should be straightforward. The spectrum of the emission, as well as the wavelength dependence of the exciting light give important insight into the nature of emitting materials. In addition to UV-Vis induced luminescence, thermally promoted chemiluminescence should also be searched for. Irradiation of solid materials often produces trapped ions, electrons and radicals which can diffuse through the medium if it is warmed. Reactions involving these diffusing species often give off a spectrum which is characteristic of the reacting species. The temperature domain over which light is emitted depends on the nature of the solid. Volatile rich ices luminesce in the 10-40K range, H₂O rich ices in the 10-150K range and higher melting point materials luminesce at much higher temperatures. Thus the monitoring of potential luminescence during core drilling and during subsequent sample warm-up is important to consider seriously as it can provide unique information on the thermal and radiation history of the sample which cannot be obtained in any other way.

Three additional spectroscopic techniques will also be summarized: Raman, NMR and ESR. Raman spectroscopy is complementary to IR spectroscopy in that it probes the vibrational frequencies of the material. It is not redundant. A good example of the power of the two techniques is provided by the spectra of interplanetary dust particles. The infrared spectra give information about the mineral components, while the Raman spectra

probe the carbon. NMR studies can tell what the fractions are of various classes of organic compounds and ESR studies can directly measure the total radical content in the ice.